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Photoexcitations in oriented tetrahexyl-sexithiophene thin films

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We report the photoexcitation properties of alkyl substituted sexithiophene thin films grown on a single crystal of potassium acid phthalate by organic molecular-beam deposition. These films possess a layered supramolecular structure with anisotropic optical properties due to the preferential molecular orientation. The poorly structured photoluminescence spectra retain the polarization properties of the absorption, which are consistent with the emission originating from the weakly interacting bulk molecules as well as from molecules at the grain boundaries rather than from immobile x traps. The layered card pack structure combined with the presence of lateral alkyl chains results in a very weak electronic coupling between oligothiophene molecules in all but one direction, namely the card pack axis. This is clearly confirmed by the photoluminescence time decay, which is very well accounted for by a one-dimensional diffusion process towards nonradiative quenching centers within the oriented crystalline domains. [S0163-1829(99)09131-6]

INTRODUCTION

It has been established that in oligothiophenes a fine tuning of the properties of interest for the applications can be achieved by a careful control of the supramolecular organization of the molecules. As a matter of fact, spatial arrangements of oligothiophenes in the solid state can considerably vary depending on the film preparation conditions and techniques.¹⁻³ With the organic molecular-beam deposition (OMBD) technique ultrathin films are fabricated by repeated stacking of monomolecular layers onto a proper substrate.⁴ Their structure results from the balance between intermolecular interactions and substrate-first monolayer interaction.⁵ For these reasons films deposited onto suitable substrates can exhibit a crystal structure which is completely different from that encountered in free standing crystals. As a consequence, optical properties and photoexcitation decays, which are very sensitive to the dipolar coupling between molecules, can be strongly affected. Also lateral substitutions within the individual molecular units can induce in the deposited film a molecular organization, which arises from the specific interactions between alkyl chains of neighbouring molecules.

Recently, a novel substituted sexithiophene (6T), namely β -tetrahexyl-sexithiophene (4H6T), possessing a center of symmetry, was synthesized. The observation of unusual crystal structures (no herringbone arrangement) for the 4H6T powders and single crystals,⁶ shows that the lateral substituents can drastically vary the supramolecular organization of the backbone with respect to unsubstituted 6T.

Thin films of 4H6T were deposited by OMBD on several substrates and under different deposition conditions and their structural and optical properties studied.^{5,7,8} Particularly in-

teresting results were obtained by using thin plates of potassium acid phthalate (KAP) as substrates for 4H6T deposition. Indeed, the films deposited on (001)-oriented KAP exhibit a peculiar supramolecular organization, where the main molecular axes of the 4H6T molecules form a 55° angle with the substrate surface and are aligned along a preferential direction, whose projection on the substrate surface lies along the b axis of the KAP unit cell.^{5,8} This peculiar supramolecular structure results in an anisotropy of the optical properties of the films revealed by optical absorption measurements performed with polarized light; nonetheless, some misalignment is present in the film, probably induced by the steric hindrance of the alkylic side chains, as revealed by oblique incidence absorption measurements.⁸

In this paper, the role of the supramolecular organization in determining the photoexcitation behavior of thin 4H6T films deposited on KAP is investigated by means of cw and time-resolved photoluminescence (PL) measurements. The results are interpreted on the basis of the previous structural and optical studies,^{5,7,8} considering in particular their dependence on light polarization and on temperature. Finally, a model for the PL time decay is assumed, which gives a deeper understanding of the excitation transfer mechanisms active in such highly oriented substituted 6T thin films.

EXPERIMENT

β -tetrahexyl-sexithiophene, shown in Fig. 1, was prepared through a self coupling of 5-bromodihexyl-terthiophene in dimethylformamide using an *in situ* prepared Ni catalyst, as reported elsewhere.^{6,9} Solutions in tetrahydrofuran (THF) with concentrations of about 10^{-5} mol/l were prepared for the time-resolved photoluminescence measurements.

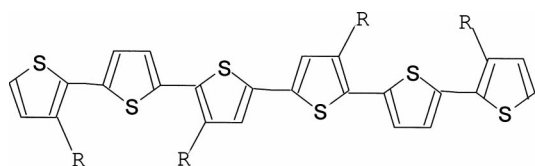


FIG. 1. Chemical structure of β -tetrahexyl-sexithiophene (4H6T). $R = C_6H_{13}$.

Deposition was performed in an OMBD apparatus⁴ using a double filament Knudsen cell and maintaining a temperature difference between the bottom of the crucible and the effusion orifice to prevent material recondensation. The crucible temperature was maintained at about 280 °C, reached after a slow heating ramp, while the substrates were kept at 25 °C during the growth. The films, of variable thickness, were deposited onto a freshly cleaved [cleavage plane (001), i.e., *ab* lattice plane] single crystal of KAP at 10^{-7} -torr base pressure with a deposition rate of 6 to 10 Å/min.

Absorption measurements were performed in the 1.5 to 4 eV spectral range using a Cary 2300 instrument at both normal and oblique incidence. Steady-state photoluminescence spectra were obtained with a SPEX 270M spectrometer equipped with a N_2 -cooled charge-coupled device (CCD) detector, by exciting with an Ar^+ laser and a monochromated Xenon lamp. Time-resolved PL measurements were performed using the second harmonic of a pulse-compressed 80-MHz Nd:YAG laser delivering 4 ps-long pulses. Temporal dispersion of the PL signal was achieved through a Hamamatsu optical sampling oscilloscope with a time resolution of 30 ps. Incident excitation intensities range from 10^{-8} to 10^{-6} J/(pulse cm^2) were used. Low-temperature measurements down to 15 K were performed using a closed circuit cryostat. Sheet polarizers were used for studying the polarization dependence of the absorbance and the photoluminescence.

RESULTS

Figure 2 shows the absorbance spectra of 5 and 86 nm-thick films deposited on KAP, taken with two perpendicular

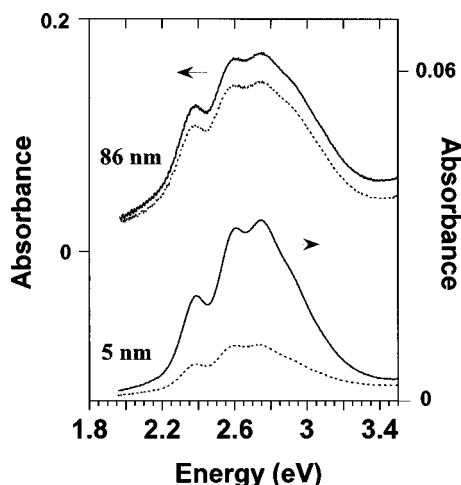


FIG. 2. Absorbance spectra of a 5 and 86 nm-thick films of 4H6T deposited on KAP for polarization of the electric field parallel (solid line) and perpendicular (dotted line) to the *b* axis of the substrate.

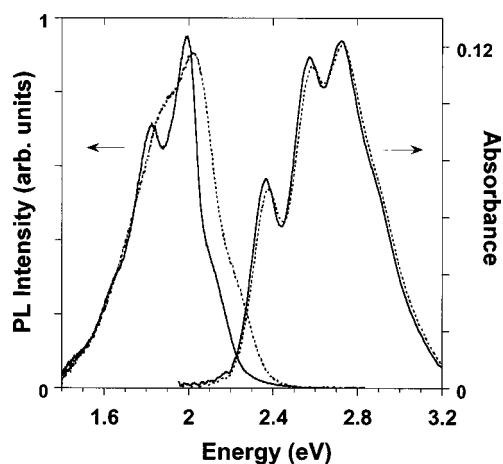


FIG. 3. Absorption and cw photoluminescence spectra of a 28 nm-thick film of 4H6T deposited on KAP at 300 K (dotted line) and 84 K (solid line).

polarizations. The maximum and minimum absorption intensities correspond to polarizations of the incident light beam with the electric field parallel and perpendicular, respectively, to the *b* axis of the KAP substrate. The projection of the main axis of the 4H6T molecules can therefore be deduced to be oriented along that axis. The optical anisotropy at the peak is about 4 for the thinner film and decreases with increasing film thickness. Considering the 55° orientation of the 4H6T molecules with respect to the substrate, absorption measurements were performed also at 35° angle of incidence to check if the film is composed by only one highly oriented single-crystalline domain. The results show only very slight variations of the anisotropy ratio with the angle of incidence, therefore suggesting that two equally populated families of crystalline microdomains probably exist, all with the molecules iso-oriented with respect to the substrate surface, but with the projection of the molecular axis in the two opposite directions along the *b* axis.⁸ The absorption spectrum exhibits its well-resolved peaks whose sharpness is surprisingly independent of temperature down to 15 K. The mean separation between the four peaks (0.18 eV) corresponds to the ring vibration, observed in the resonant Raman spectrum, mostly coupled to the electronic transition,¹⁰ suggesting that a vibronic replica is involved. On the other hand, even though all the vibronic peaks exhibit the same temperature independence, their relative intensity can not be fitted with the Poisson distribution, which should result from the electron-vibrational coupling.

Figure 3 shows the absorption and cw photoluminescence spectra of a 28 nm-thick film. At room temperature the PL spectrum shows poorly resolved vibronic side bands, which become better resolved at low temperature, again with 0.18 eV separation. The PL spectrum (measured far from the film edges) is independent of the sample position and the excitation energy even upon fine tuning of the exciting light around the onset of the absorption band down to 2.17 eV, thus indicating that no mobility edge is detected for this film. On the other hand, the PL spectrum measured near the film edges shows an additional blueshifted component revealing the coexistence of two phases. This additional component is only observed by exciting at energies above 2.4 eV, as

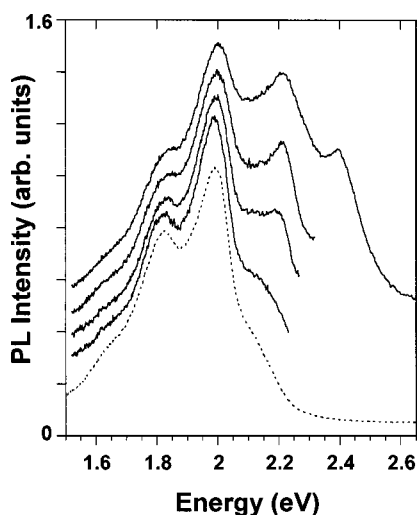


FIG. 4. PL of 4H6T film at $T = 84$ K obtained by exciting at the film edges (solid lines) for different excitations (2.82, 2.45, 2.42, and 2.38 eV from top to bottom). The PL spectrum of the bulk film (dashed line) is reported for comparison (excitation energy 2.75 eV). The PL intensities are normalized and the spectra are displaced vertically for clarity.

shown in Fig. 4, indicating that 4H6T molecules located at the film edges possess higher energy absorption and emission properties. These results are in agreement with a more distorted conformation of the 4H6T molecules at the edges of the film with respect to those in the bulk, and with the fact that the larger disorder present at the sample boundaries causes a localization of the excitation, thus preventing its migration towards lower energy levels. In the discussion of the following section only the bulk data will be considered.

The PL decay of the 4H6T film is reported in Fig. 5 at 300 K, together with the decay of the PL of the 4H6T solution. While the solution shows an exponential decay with a lifetime of about 1 ns (see the least square fit in Fig. 5), for the film a more complex behavior is observed. The temporal dynamics was found to be independent of the laser intensities used in the experiment. The initial fast decay shows a non exponential behavior. The decay rate depends on the position of the sample, indicating that the faster decrease of the PL intensity in the films with respect to 4H6T in solution is related to the presence of an inhomogeneous density profile of quenching traps. At longer times the decay slows down, with typical decay times somewhat longer (1.4–1.8 ns) than that observed in solution. By considering the interpulse time (12.5 ns) of our experiment and the exciton lifetime (1 ns), the extent of the excitonic population due to repeated excitation does not influence the temporal dynamics of the photoluminescence. So we believe that the long time decay of the films should be related to more complex deactivation pathways or other emitting species (e.g., excimer states). Finally, we have found a negligible dependence (in the range of the variations observed for different sample positions) of the PL temporal decay on temperature (from 15 to 300 K).

The polarization properties of the PL of the 28 nm-thick film are reported in Fig. 6. The excitation polarization is along the b axis of the KAP, while the emitted light is analyzed parallel and perpendicular to this direction. The cw PL spectrum shows an average anisotropy of 2.5 within a 20%

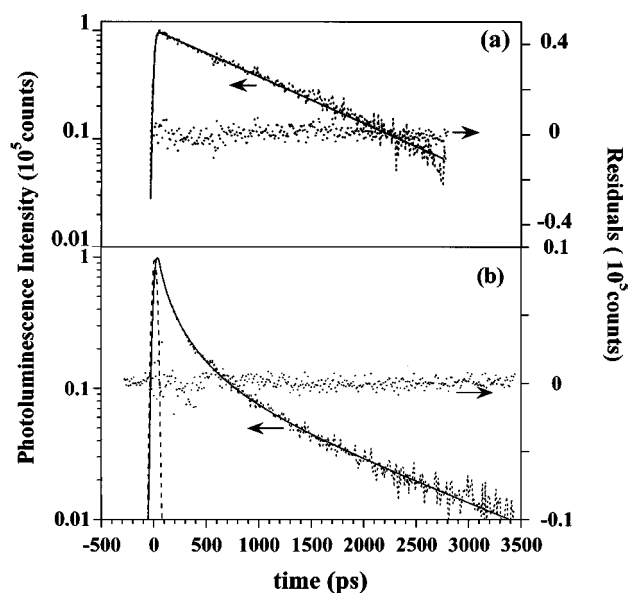


FIG. 5. PL time decay of 4H6T in THF solution (a) and of a 28 nm-thick film deposited on KAP (b) at 300 K. Exciting energy is 4.66 eV for the solution and 2.33 eV for the film. The best least square fits (solid line) are reported for the solution (exponential with $\tau = 1040$ ps) and for the film [from Eq. (3), $B/A = 2.7 \times 10^{-2}$; $\tau_d = 7$ ps; $t_1 = 1400$ ps] with the residuals (data points). The time response of the instrument is also shown for the film (dashed line).

variations, due to sample inhomogeneity and/or scrambling effects induced by the KAP substrate, observed by varying the sample position. The time resolved PL data (see inset of Fig. 6) show that the two components of the emission exhibit exactly the same temporal decay in the whole measured time range, with no loss of the polarization memory.

DISCUSSION

The body of data presented in the previous section are well accounted for by the supramolecular organization reported in Fig. 7, consisting of mono-molecular layers stacked

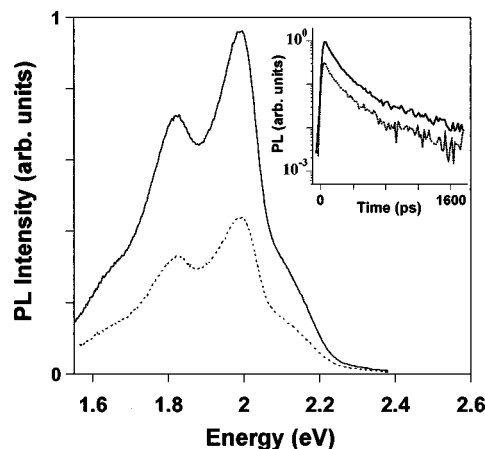


FIG. 6. Polarized PL of a 28 nm-thick film of 4H6T deposited on KAP measured at 84 K (excitation 2.71 eV). In the insert the polarized PL time decay measured at 300 K (excitation 2.33 eV) is reported. The excitation light is polarized along the b axis of the KAP. PL is analyzed parallel (solid line) and perpendicular (dashed line) to this direction.

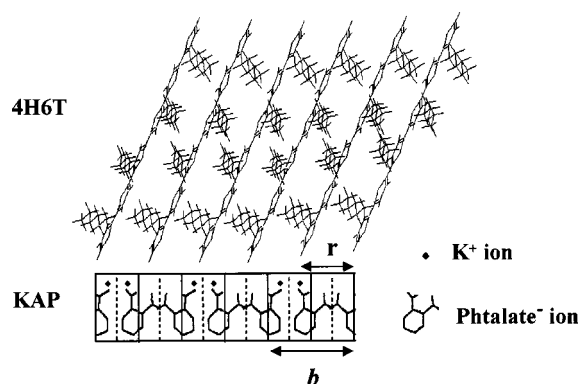


FIG. 7. Model of the structure of 4H6T films on KAP. Note the commensurate spacing of 4H6T and KAP lattices along the b direction, where $5r = 3b$.

one on top of the other. Within each individual layer the molecular planes of the conjugated backbones are separated by 5.78 Å, as derived from the packing of the smectic phase,⁶ with a card pack arrangement whose axis forms an angle of 55° with respect to the molecular long axis. The preferential orientation of the molecular axis, which is deduced from the optical dichroism, is driven by the interaction between the organic substrate and the first monomolecular layer, possibly via either potassium and carboxylic ions close to the surface of the cleavage plane, or π interactions of phenyl residues, just below, which are inclined by 69° with respect to the cleaved surface.¹¹ Indeed, in the case of growth on KAP, a commensurability between the overgrown layer and the substrate is attained. Figure 7 shows that five 4H6T chains (intermolecular distance $r = 5.78$ Å) are exactly accommodated into three translations along the KAP b axis ($b = 9.60$ Å).

The fact that the absorption spectrum is quite insensitive to the temperature is a clear indication that the structure previously described is stable within a wide temperature range and the conformation of the molecules is planar even at room temperature. The absorption spectrum lacks of the broad high-energy peak which is usually attributed to the molecular excitons formed by the interaction between molecular transition moments.^{3,12–14} In unsubstituted 6T this peak has been observed at about 3.5 eV.¹⁴ The absence of the exciton peak can be explained by considering that, in the peculiar structure observed in our samples, the distance between parallel transition dipoles is 5.78 Å and the molecular transition dipoles are inclined of 55° with respect to the card pack axis yielding a very small excitonic resonance interaction.

The peak position of the cw PL corresponds quite well to that of the unsubstituted crystalline 6T, this being consistent with the planar conformation of the molecules of the film. Moreover, the lack of any dependence of the emission spectrum on the excitation energy, which also indicates the lack of a detectable mobility edge, is consistent with the good structural order of the sample and with the absence of deep x traps as preferred emitting states. The poorly structured shape of the cw emission spectrum could be related to the fact that, as it will be discussed below, the excitation migrates along the card pack axis without being trapped at a specific site and therefore the emission can take place from any of the molecules visited by the excitation, with a conse-

quent distribution of emitting energies. We note that the properties of the steady state PL of these films completely differ from those of both unsubstituted and α,ω -substituted 6T films or single crystals so far reported in the literature^{3,15,16} since in those cases the PL, mainly due to x -trap emission, strongly depends on the type and concentration of the specific traps in the film, thus generally displaying properties which depend on the excitation energy.

The intermolecular transfer of the excitation towards randomly distributed nonradiative quenching centers can explain the initial fast nonexponential decay of the PL signal. According to the diffusion model,¹⁷ the particle density decay in the long time approximation follows a stretched exponential law of the type $\exp[-t^{d/(d+2)}]$ in d dimension. The molecular card pack arrangement inferred by the diffraction analysis (see Fig. 7) suggests that the intermolecular excitation transfer should occur preferentially within each individual stack of molecules along the b direction. As a matter of fact, the particular molecular arrangement obtained in this film yields a two dimensional confinement within the monomolecular layers parallel to the substrate with the additional confinement due to the regular arrangement of the lateral molecular substituents. As a result, the hopping motion of the excitations is essentially restricted along the projection of the thiophene backbones (b axis). Following the results obtained by Grassberger and Procaccia¹⁸ on the diffusion of a density of particles moving in one dimension with a diffusion constant D , in a medium with a concentration of static absorbing traps n_s , the decay law of the PL intensity $I_0(t)$ can be written as

$$I_0(t) \approx \frac{2\sqrt{\pi}}{3n_s} \left(\frac{t}{\tau_d} \right)^{1/6} \exp\left(-\frac{t}{\tau_d}\right)^{1/3} \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

$$\tau_d = \frac{4}{27\pi^2 D n_s^2}, \quad (2)$$

where τ_d is the diffusion time constant and τ is the decay time of the 4H6T isolated molecule. According to Eq. (1), the decay rate of the luminescence intensity should be that of the isolated molecule in the long time limit. Indeed, by assuming the decay time τ as measured for the solution ($\tau = 1$ ns), the decay of the PL in the whole time range can be obtained by the sum of the fast decay of diffusion quenched excitons [Eq. (1)] and a slow exponential term to account for the weak-long time emission:

$$I(t) \approx A \left(\frac{t}{\tau_d} \right)^{1/6} \exp\left(-\frac{t}{\tau_d}\right)^{1/3} \exp\left(-\frac{t}{\tau}\right) + B \exp\left(-\frac{t}{t_1}\right). \quad (3)$$

The fitting curves obtained with Eq. (3), reported in Fig. 5, are a least square fit to the experimental data using a convolution routine to eliminate the instrumental response. A value of $\tau_d \approx 1 \div 5 \times 10^{-11}$ s is inferred, which compares favorably with values of the diffusion time reported in literature for thiophene-based compounds.¹⁹ We have found that the exponential contribution to the PL intensity, probably associated to emission from molecules located at the grain boundaries, is rather weak ($B/A \sim 6 \times 10^{-3} \div 2 \times 10^{-2}$), and has a negligible influence on the determination of τ_d . The

short-time behavior of the PL decay is fully accounted for by Eq. (1) up to about 600 ps. In this short-time region, we therefore consider that molecular emission during monodimensional diffusion is the main contribution to the observed PL. The independence of the decay law from the laser intensity rules out that nonradiative quenching arises from collisions between singlet excitons and other photogenerated species (interchain polarons) or exciton-exciton annihilation, but rather is indicative of the fact that impurities and/or structural defects are the main nonradiative decay channels. Using the value of $D = 6 \times 10^{-3} \text{ cm}^2/\text{s}$, obtained through optical measurements on polycrystalline 6T films,²⁰ we infer an average concentration of quenching defects of about $1 \div 2\%$, depending on the position of the sample.

The lack of any change in the decay law upon changing the polarization of the emitted light is indicative of the fact that no change of polarization takes place upon intermolecular hopping within the crystalline grains before the radiative emission takes place. A rough evaluation of the lower limit of the linear size r_{\min} of the crystallites, obtained from the diffusion equation $r_{\min}^2 = Dt$ with $t = 600 \text{ ps}$, yields a value $r_{\min} \approx 200 \text{ \AA}$. It is also worth mentioning that the PL anisotropy is maintained for times longer than those involved in the purely diffusive motion. This is indicative of the fact that emission takes place from the same crystalline domains that are excited and the fraction of excitations that eventually emit from the boundaries of the crystalline domains does not produce scrambling of the cw PL polarization.

The photoexcitation scenario of the film of 4H6T here presented is much different from that encountered in films and single crystals of unsubstituted oligothiophenes.^{14,21,22} Indeed in unsubstituted conjugated oligomers, which display short interchain distances in the solid state, the strong intermolecular interactions lead to a blueshift of the lowest optical allowed transition while the transition from the lowest excited state to the ground state has no oscillator strength.²³ As a consequence, the photoluminescence of the films is mainly produced by traps. Differently, in this substituted 6T the weakly interacting molecules constituting the crystalline lattice are responsible for the observed emission. Time-resolved photoluminescence data indicate that the main con-

tribution in the PL is due to molecular emission governed by a one-dimensional diffusion motion without trapping by immobile emissive centres.

CONCLUSIONS

In this paper, we have demonstrated that layer by layer deposition on suitable, clean and well-defined substrate yields oligothiophene films of controlled structural order and desired thickness, therefore suitable for transmission optical measurements. Even though the steric hindrance exerted by the lateral alkyl side chains limits the degree of molecular alignment, fairly anisotropic thin films of substituted sexithiophenes have been obtained by repeated stacking of monomolecular layers onto a KAP substrate in high vacuum. The orientation properties of the substrate possibly arise from the π interaction between the conjugated ring of the phthalate ion (surfacing at the cleavage plane) and the thiophene rings of the first overgrown layer.

On the basis of the optical data we have proposed that the excitonic interactions are reduced, with respect to unsubstituted molecules, by the increased backbone distance and the PL emission occurs from the weakly interacting bulk molecules as well as from molecules at the grain boundaries rather than from immobile x traps. The PL decay dynamics is accounted for by a one-dimensional diffusion process towards nonradiative quenching centers in the direction of the b KAP axis, consistently with the peculiar card pack molecular arrangement attained in these films. Radiative recombination occurs mainly within the same oriented domains which are excited, whose lower limit size could be estimated of about 20 nm.

In conclusion, our results show that the preparation of properly β -substituted oligothiophene films of controlled structural order represents a good approach to improve the photoluminescence efficiency of oligothiophene films and allows to obtain polarized emission.

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